

# Does a surface attached globule phase exist ?

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## Abstract

A long flexible neutral polymer chain immersed in a poor solvent and interacting with an impenetrable attractive surface exhibits a phase known as surface attached globule (**SAG**) in addition to other adsorbed and desorbed phases. In the thermodynamic limit, the **SAG** phase has the same free energy per monomer as the globular phase, and the transition between them is a surface transition. We have investigated the phase diagrams of such a chain in both two- and three- dimensions and calculated the distribution of monomers in different domains of the phase diagram.

*Key words:* Surface attached globule(**SAG**) phase; Exact enumeration.

*PACS:* 64.60.-i, 68.35.Rh, 5.50.+q

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A long flexible neutral polymer chain immersed in a poor solvent and interacting with an impenetrable surface is known to exhibit a very rich phase diagram [1]. Competition between the lower internal energy near an attractive wall and higher entropy away from it results in a transition, where for a strongly attractive surface the polymer sticks to the surface and for weak attraction the polymer chain remains desorbed. On the other hand, due to the self-attraction in the polymers the possibility of a collapse transition both in the desorbed and adsorbed states occur. The phase diagram is generally plotted in variables  $\omega = e^{\beta\epsilon_s}$  and  $u = e^{\beta\epsilon_u}$  where  $\beta$  is the inverse temperature,  $\epsilon_s$  is the (attractive) energy associated with each monomer lying on the surface and  $\epsilon_u$  represents an attractive interaction energy between pairs of monomer which come close to each other and are separated along the chain by more than one unit. The short range repulsion between the monomer is taken in a lattice model by self-avoidance [2]. Considerable attention has been paid to find the full phase diagram of such a chain in both two dimensions ( $2D$ ) and three dimensions ( $3D$ ).

In one of the earliest papers on the subject, Bouchaud and Vannimenus [3] derived the exact phase diagram on a  $3D$ -Sierpinski gasket. The phase dia-

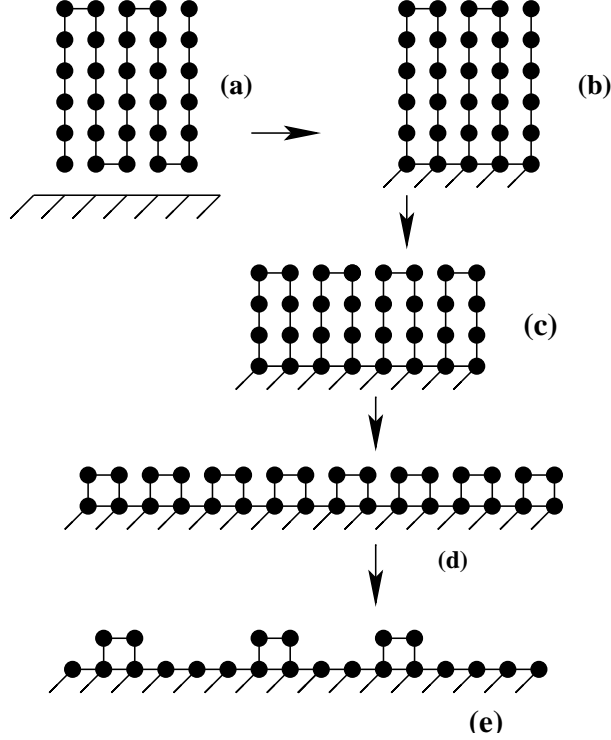


Fig. 1. Schematic diagrams of self-avoiding walk conformation at  $T=0$ . Below critical value  $\omega_{c1}$ , (a) the number of monomers at the surface are zero and polymer is in the desorbed state; (b) the structure shown in Fig.(a) gets adsorbed on the surface at critical value  $\omega_{c1}$ . Average number of pair of neighbouring monomers on the surface  $\langle N_c \rangle$  scales as  $N^{d-1}$ ; (c)  $\langle N_c \rangle$  increases with  $\omega$ ; (d) At  $\omega_{c2}$ ,  $\langle N_c \rangle$  is maximum; (e)  $\langle N_c \rangle$  decreases sharply with further increase in  $\omega$ .

gram consisted of the adsorbed expanded (**AE**), desorbed expanded (**DE**) and desorbed collapsed (**DC**) phases. Kumar and Singh [4] have reinvestigated the phase diagram for 3D-Sierpinski gasket and showed that for a certain range of surface interactions, an additional phase having the feature of globule attached to the surface exists. Recently Singh et.al. [5,6] using extrapolation of exact series expansions calculated the phase diagram for the polymer chain in both 2D and 3D (Euclidean) space. These phase diagrams show the existence of the surface attached globule (**SAG**) phase in qualitative agreement with the one found earlier for the gasket. It is important to note that in the thermodynamic limit, the **SAG** phase has the same free energy per monomer as the **DC** phase, and the transition between them is a surface transition.

As shown earlier [1], it is easy to understand the **SAG** and its boundary in the limit  $T = 0$ . At  $T = 0$ , the polymer configurations may be mapped by Hamiltonian walk as shown in Fig 1(a). Its bulk energy is the same as in the **DC** phase and the surface energy is  $(\epsilon_u - \epsilon_s)L_{\parallel}^{d-1} + (d-1)\epsilon_u N/L_{\parallel}$ . Minimizing the surface energy with respect to  $L_{\parallel}$ , we obtain

$$E_{\text{SAG}} = -(d-1)\epsilon_u N + d\epsilon_u^{\frac{d-1}{d}} (\epsilon_u - \epsilon_s)^{\frac{1}{d}} N^{\frac{d-1}{d}}. \quad (1)$$

While for the **DC** phase,

$$E_{\text{DC}} = -(d-1)\epsilon_u N + d\epsilon_u N^{\frac{d-1}{d}}. \quad (2)$$

In the **AC** phase, we have  $L_{\perp} = 1$ ,  $L_{\parallel} = N^{1/(d-1)}$ , and the free energy at  $T = 0$  is

$$E_{\text{AC}} = -(d-2)\epsilon_u N - \epsilon_s N + (d-1)\epsilon_u N^{\frac{d-2}{d-1}}. \quad (3)$$

Comparing the energies of these phases, we see that **SAG** phase has lower free energy than the **DC** or the **AC** phases for  $0 \leq \epsilon_s \leq \epsilon_u$ . Thus the lower and upper boundaries of the **SAG** phase (lines  $\omega_{c1}$  and  $\omega_{c2}$  in Fig.2) tend to  $\omega_{c1} = 1$  and  $w_{c2} = u$  for large  $u$ .

In the case of partially directed polymer in  $2D$  we have found [1] exact phase diagram of the **SAG** phase. In this case the polymer has different behaviour depending on whether it is near the wall perpendicular to the preferred direction (**SAG1**) or the wall is parallel to the preferred direction (**SAG2**). The phase boundaries of **SAG1** and **SAG2** have been found by calculating this orientation dependent surface energy.

Since the analytical approach are limited to very few cases such as fractal lattices or the directed walks on  $2D$  lattices, we have to resort to numerical methods to calculate the phase diagram in other cases. A lattice model using extrapolation of exact series expansions (herein after referred to exact enumeration method) has been found to give satisfactory results as it takes into account the corrections to scaling. To achieve the same accuracy by the Monte Carlo method, a chain of about two order magnitude larger than in the exact enumeration method has to be considered [7].

In this article we report our results which we have found using exact enumeration method both for  $2D$  and  $3D$  cases. Let  $C_N(N_s, N_u)$  be the number of SAWs of  $N$  sites having  $N_s$  monomers on the surface and  $N_u$  nearest neighbour monomer pairs. We analyzed the series for  $C_N(N_s, N_u)$  up to  $N = 30$  for square lattice and  $N = 20$  for the cubic lattice; thus extending the series by two more terms in both cases.

To obtain better estimates of critical points as well as the phase boundaries, we extrapolate for large  $N$  using ratio method [8]. Let

$$Z_N(\omega, u) = \sum_{N_s, N_u} C_N(N_s, N_u) \omega^{N_s} u^{N_u}, \quad (4)$$

be the partition function. Then, the reduced free energy per monomer can be

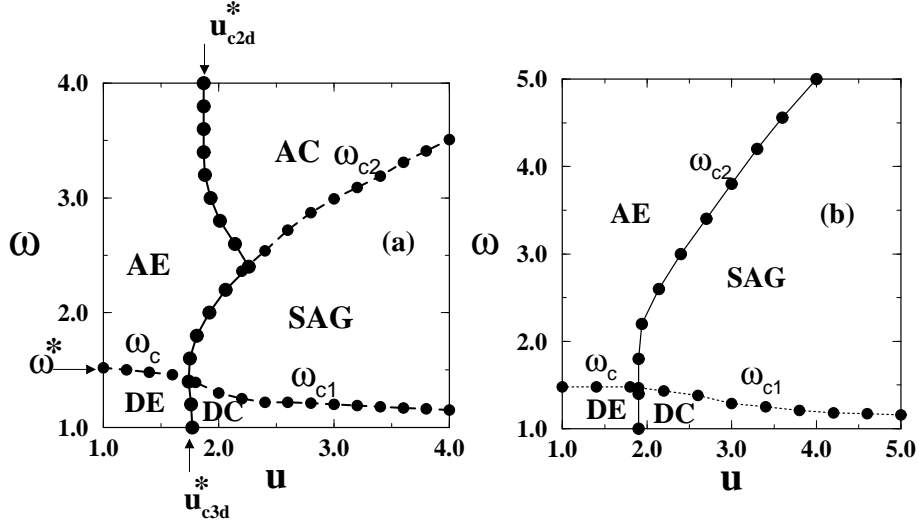


Fig. 2. This figure shows the phase diagram of a surface interacting linear polymer in 3D and 2D space respectively. The transition lines were obtained using method of exact-enumeration.

written as [8]

$$G(\omega, u) = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_N(\omega, u). \quad (5)$$

The phase boundaries are then found from the maxima of  $\frac{\partial^2 G(\omega, u)}{\partial \epsilon_s^2}$  ( $= \frac{\partial \langle N_s \rangle}{\partial \epsilon_s}$ ) and  $\frac{\partial^2 G(\omega, u)}{\partial \epsilon_u^2}$  ( $= \frac{\partial \langle N_u \rangle}{\partial \epsilon_u}$ ).

The phase diagram thus obtained is shown in Fig.2(a) for three dimensions. It has five phases which are denoted as desorbed expanded (**DE**), desorbed collapsed (**DC**), adsorbed expanded (**AE**), adsorbed collapsed (**AC**) and surface attached globule (**SAG**). Since in case of two dimensions, surface is a line, therefore, we do not find adsorbed collapsed phase [Fig2(b)]. The value of  $u_c$  at  $\omega = 1$  is found to be  $1.93 \pm 0.02$  and  $1.76 \pm 0.02$  for 2D and 3D, respectively. The value of  $\omega_c$  at  $u = 1$  is found to be  $2.05 \pm 0.01$  and  $1.48 \pm 0.02$  for 2D and 3D, respectively. The special adsorption line  $\omega_c$  separates the **AE** phase from that of **DE** phase. The  $u_c$  line meets  $\omega_c$  line which is a multi-critical point  $(u_c, \omega_c) = (1.93, 1.46)$  for 2D and  $(1.76, 1.38)$  for 3D, respectively. Values of 3D are same as those reported by us earlier [1]. The value of critical exponents both at the ordinary and multi-critical points are in very good agreement with the known results [?].

In order to show how the monomers distribute when the chain is in the different regimes of the phase diagram, we calculate the value of each term in

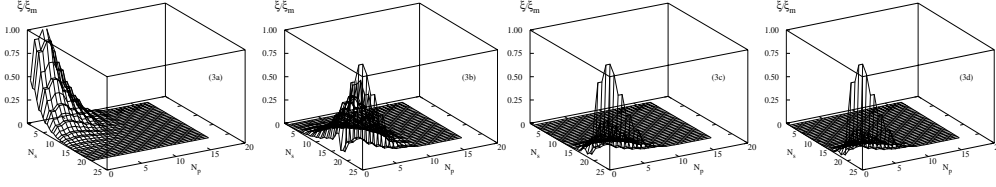


Fig. 3. Plot of  $\xi/\xi_m$  as a function of  $N_s$  and  $N_p$ . Here  $\xi = C_N(N_s, N_p)\omega^{N_s}u^{N_p}$  and  $\xi_m$  is the maximum value of  $\xi$  for a given value of  $\omega$  and  $u$ . (a)  $u = 1.0$ ,  $\omega = 1.0$ ; (b)  $u = 1.0$ ,  $\omega = 2.0$ ; (c)  $u = 1.0$ ,  $\omega = 3.0$ ; (d)  $u = 1.0$ ,  $\omega = 3.5$

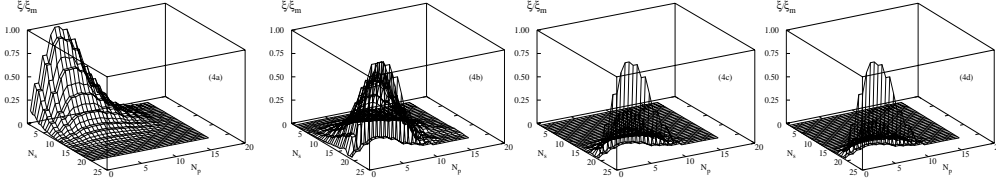


Fig. 4. Same as Fig.3, (a)  $u = 1.5$ ,  $\omega = 1.0$ ; (b)  $u = 1.5$ ,  $\omega = 2.0$ ; (c)  $u = 1.5$ ,  $\omega = 3.0$ ; (d)  $u = 1.5$ ,  $\omega = 3.5$

Eq.(4) for given values of  $u$  and  $\omega$  and plot the results for walk up to 20 steps (3D case only) in Fig.(3-6). Here we have plotted  $\xi/\xi_m$  for eight values of  $\omega$ , where  $\xi = C_N(N_s, N_u)\omega^{N_s}u^{N_u}$  ( $\xi_m$  being the maximum value of  $\xi$ ) as a function of  $N_s$  and  $N_u$ . Since the term which contribute most to the sum of Eq.(4) represents the most probable configurations of the chains, we can infer, from these figures about the manner in which the monomers are distributed in different states. For example, Fig.(3(a-d) and 4(a-d)) show how the distribution of monomers changes as  $\omega$  is varied at fixed  $u = 1.0$  and  $1.5$  (corresponding to expanded state). It is clear from these figures (3(a) and 4(a)) that  $N_s$  and  $N_u$  are nearly zero around  $\omega = 1$ . In Fig.(3(d)-4(d)), at  $\omega = 3.5$ ,  $N_s$  is around 20 corresponding to the adsorbed expanded state of chain. For  $u = 2.0$  and  $2.5$  (corresponding to the collapsed state), distribution is shown in Fig.(5(a-d) and 6(a-d). For  $\omega = 1$ , the polymer chain is in the bulk as there is any monomer on the surface ( $N_s \sim 0$ ) but  $N_u$  is large which indicate that monomers occupy the neighbouring sites. When  $\omega$  is chosen equal to 2.0 a value which lies in between  $\omega_{c1}$  and  $\omega_{c2}$  line, as shown in Fig.2, a fraction of monomers gets attached to the surface ( $N_s \sim 12$ ) indicating the breaking of translational invariance of the globule corresponding to the **SAG** phase. With further increase in  $\omega$  polymer gets adsorbed in collapsed state where  $N_s \sim 20$  and  $N_u$  is around 8.

We also calculate number of neighbouring pairs of monomers at the surface *i.e.*  $\langle N_c \rangle$ . This can be calculated from the expression

$$\langle N_c \rangle = \frac{\sum N_c Z_N(\omega, u)}{\sum Z_N(\omega, u)} \quad (6)$$

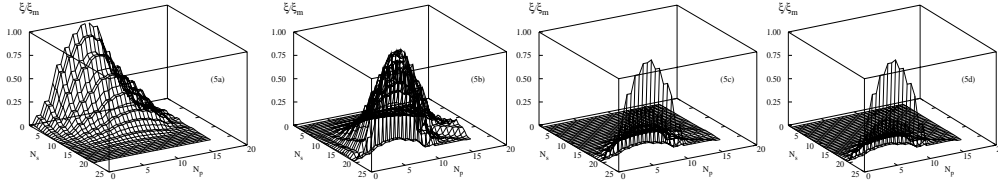


Fig. 5. Same as FIG.3, (a)  $u = 2.0$ ,  $\omega = 1.0$ ; (b)  $u = 2.0$ ,  $\omega = 2.0$ ; (c)  $u = 2.0$ ,  $\omega = 3.0$ ; (d)  $u = 2.0$ ,  $\omega = 3.5$

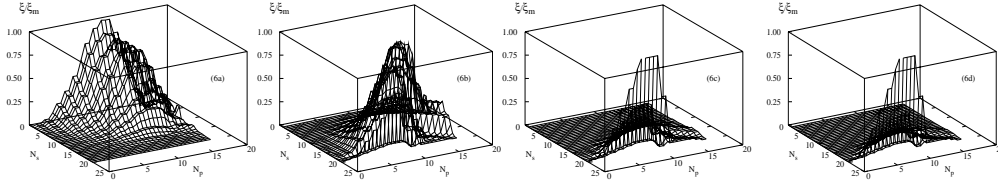


Fig. 6. Same as FIG.3, (a)  $u = 2.5$ ,  $\omega = 1.0$ ; (b)  $u = 2.5$ ,  $\omega = 2.0$ ; (c)  $u = 2.5$ ,  $\omega = 3.0$ ; (d)  $u = 2.5$ ,  $\omega = 3.5$

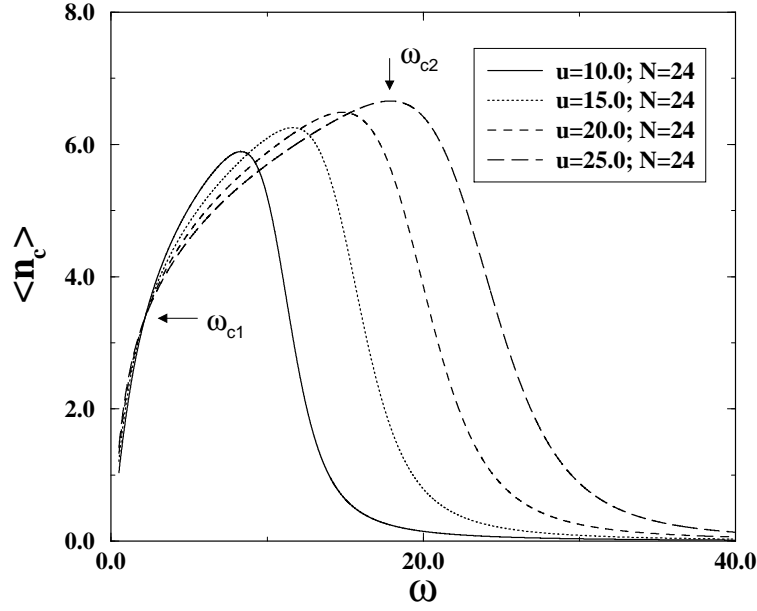


Fig. 7. Diagram shows the variation of number of monomer pairs on the surface  $\langle N_c \rangle$  with  $\omega$ .

The variation of  $\langle N_c \rangle$  with  $\omega$  for different value of  $u = 10, 15, 20, 25$  is shown in Fig.7 for two dimensions. At such a high value of  $u$  the most likely structure is of Hamiltonian walk as shown in Fig.1(a). Below certain value of  $\omega_{c1}$ , this structure remains in bulk and  $\langle N_c \rangle$  and  $\langle N_s \rangle$  are almost zero. At certain critical value  $\omega_{c1}$ , this structure gets stuck on the surface (Fig.1(b)).

At this value of  $\omega$ , the  $\langle N_c \rangle$  is equal to  $\langle N_s \rangle$  and goes as  $N^{d-1}$ . As  $\omega$  increases  $\langle N_c \rangle$  also increases and reaches to its maximum at  $\omega_{c2}$ . The corresponding configuration is shown in Fig.1(d). With further increase in  $\omega$ , polymer gets adsorbed on the surface with decrease in  $\langle N_c \rangle$  as shown in Fig.7 and Fig.1(e).

The results given above should provide ample evidences in favour of the existence of the **SAG** phase. The phase boundaries  $\omega_{c1}$  and  $\omega_{c2}$  tend to 1 and  $u$  respectively as  $T$  goes to zero and is independent of dimension. We once again emphasized that the transition associated with  $\omega_{c1}$  line is surface transition.

We thank Deepak Dhar and R. Rajesh for many helpful discussions. We would also like to thank the organizers for giving us opportunity to present this work. Financial assistance from *INSA*, New Delhi and *DST*, New Delhi are acknowledged.

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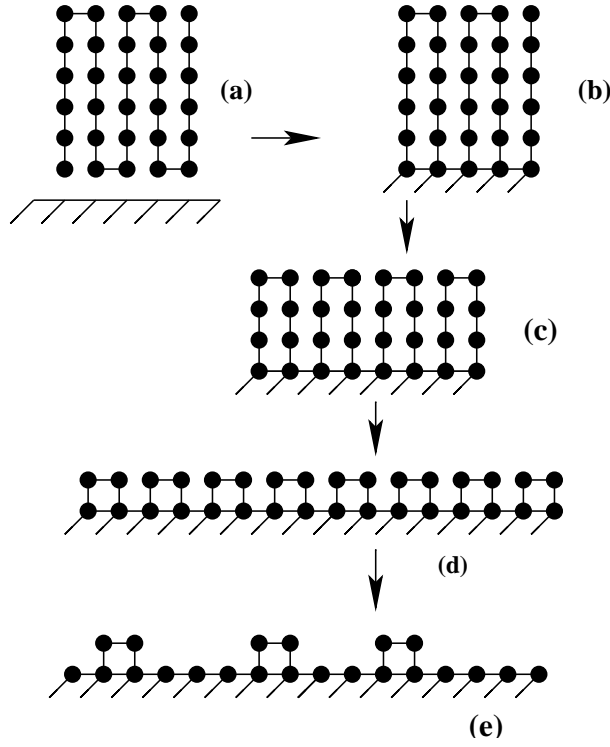


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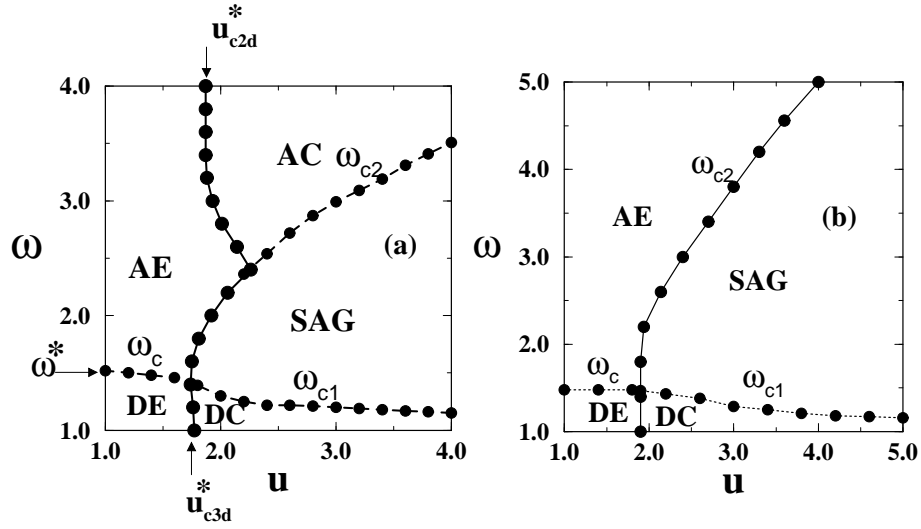


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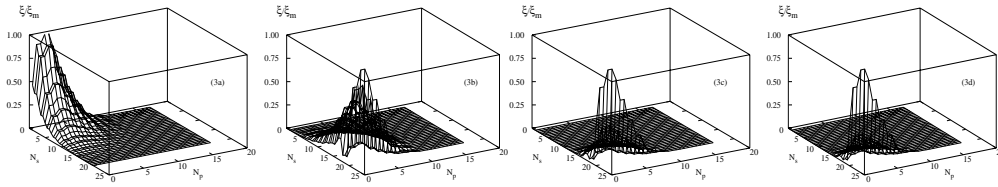


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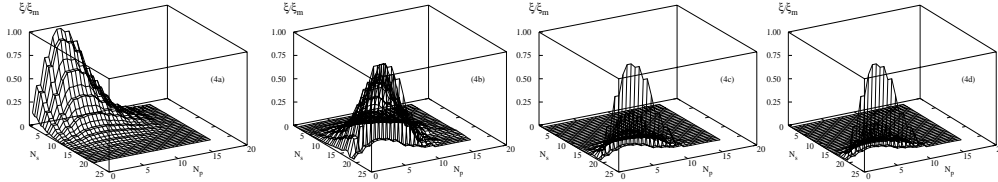


Fig. 4. Same as Fig.3, **(a)**  $u = 1.5$ ,  $\omega = 1.0$ ; **(b)**  $u = 1.5$ ,  $\omega = 2.0$ ; **(c)**  $u = 1.5$ ,  $\omega = 3.0$ ; **(d)**  $u = 1.5$ ,  $\omega = 3.5$

Eq.(4) for given values of  $u$  and  $\omega$  and plot the results for walk up to 20 steps (3D case only) in Fig.(3-6). Here we have plotted  $\xi/\xi_m$  for eight values of  $\omega$ , where  $\xi = C_N(N_s, N_u)\omega^{N_s}u^{N_u}$  ( $\xi_m$  being the maximum value of  $\xi$ ) as a function of  $N_s$  and  $N_u$ . Since the term which contribute most to the sum of Eq.(4) represents the most probable configurations of the chains, we can infer, from these figures about the manner in which the monomers are distributed in different states. For example, Fig.(3(a-d) and 4(a-d)) show how the distribution of monomers changes as  $\omega$  is varied at fixed  $u = 1.0$  and  $1.5$  (corresponding to expanded state). It is clear from these figures (3(a) and 4(a)) that  $N_s$  and  $N_u$  are nearly zero around  $\omega = 1$ . In Fig.(3(d)-4(d)), at  $\omega = 3.5$ ,  $N_s$  is around 20 corresponding to the adsorbed expanded state of chain. For  $u = 2.0$  and  $2.5$  (corresponding to the collapsed state), distribution is shown in Fig.(5(a-d) and 6(a-d). For  $\omega = 1$ , the polymer chain is in the bulk as there is any monomer on the surface ( $N_s \sim 0$ ) but  $N_u$  is large which indicate that monomers occupy the neighbouring sites. When  $\omega$  is chosen equal to 2.0 a value which lies in between  $\omega_{c1}$  and  $\omega_{c2}$  line, as shown in Fig.2, a fraction of monomers gets attached to the surface ( $N_s \sim 12$ ) indicating the breaking of translational invariance of the globule corresponding to the **SAG** phase. With further increase in  $\omega$  polymer gets adsorbed in collapsed state where  $N_s \sim 20$  and  $N_u$  is around 8.

We also calculate number of neighbouring pairs of monomers at the surface *i.e.*  $\langle N_c \rangle$ . This can be calculated from the expression

$$\langle N_c \rangle = \frac{\sum N_c Z_N(\omega, u)}{\sum Z_N(\omega, u)} \quad (6)$$

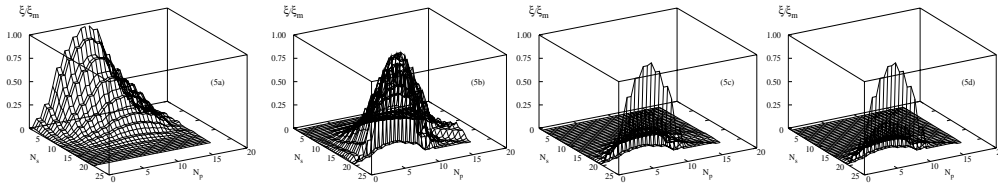


Fig. 5. Same as FIG.3, (a)  $u = 2.0$ ,  $\omega = 1.0$ ; (b)  $u = 2.0$ ,  $\omega = 2.0$ ; (c)  $u = 2.0$ ,  $\omega = 3.0$ ; (d)  $u = 2.0$ ,  $\omega = 3.5$

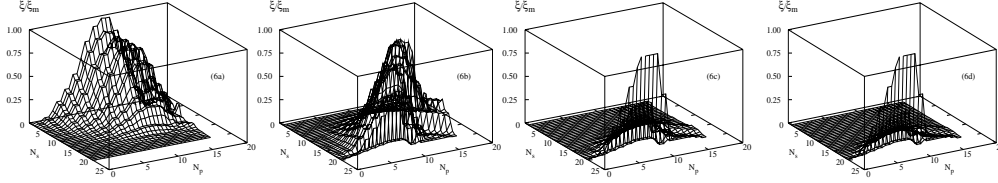


Fig. 6. Same as FIG.3, (a)  $u = 2.5$ ,  $\omega = 1.0$ ; (b)  $u = 2.5$ ,  $\omega = 2.0$ ; (c)  $u = 2.5$ ,  $\omega = 3.0$ ; (d)  $u = 2.5$ ,  $\omega = 3.5$

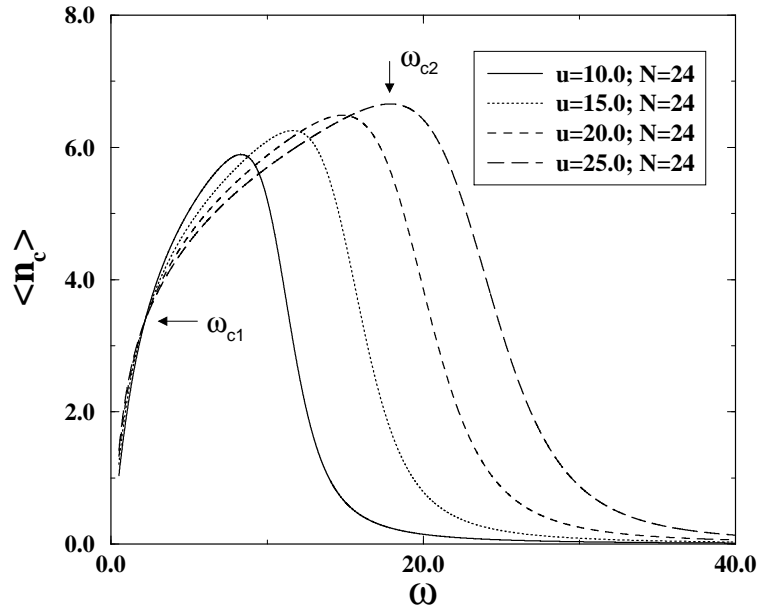


Fig. 7. Diagram shows the variation of number of monomer pairs on the surface  $\langle N_c \rangle$  with  $\omega$ .

The variation of  $\langle N_c \rangle$  with  $\omega$  for different value of  $u = 10, 15, 20, 25$  is shown in Fig.7 for two dimensions. At such a high value of  $u$  the most likely structure is of Hamiltonian walk as shown in Fig.1(a). Below certain value of  $\omega_{c1}$ , this structure remains in bulk and  $\langle N_c \rangle$  and  $\langle N_s \rangle$  are almost zero. At certain critical value  $\omega_{c1}$ , this structure gets stuck on the surface (Fig.1(b)).

At this value of  $\omega$ , the  $\langle N_c \rangle$  is equal to  $\langle N_s \rangle$  and goes as  $N^{d-1}$ . As  $\omega$  increases  $\langle N_c \rangle$  also increases and reaches to its maximum at  $\omega_{c2}$ . The corresponding configuration is shown in Fig.1(d). With further increase in  $\omega$ , polymer gets adsorbed on the surface with decrease in  $\langle N_c \rangle$  as shown in Fig.7 and Fig.1(e).

The results given above should provide ample evidences in favour of the existence of the **SAG** phase. The phase boundaries  $\omega_{c1}$  and  $\omega_{c2}$  tend to 1 and  $u$  respectively as  $T$  goes to zero and is independent of dimension. We once again emphasized that the transition associated with  $\omega_{c1}$  line is surface transition.

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